Orbital Dependent Superconductivity in Sr_2RuO_4

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We show that for superconducting Sr_2RuO_4 any unconventional pairing in the part of the Fermi surface with Ru $4d_{xy}$ orbital character is weakly coupled to that with Ru $\{4d_{xz}, 4d_{yz}\}$ orbital character. This naturally gives rise to two disparate energy scales in the superconducting state which leads to novel low temperature properties in a variety of thermodynamic and transport properties and which would also account for the large residual density of states seen in specific heat and nuclear quadrapole resonance measurements. [S0031-9007(97)03076-7]

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Sr_2RuO_4 provides the first example of a layered perovskite material that exhibits superconductivity without the presence of copper [1]. Even though there is a close structural similarity with the high T_c materials, the electronic properties are very different. While it is clear that electron correlation effects are important in Sr_2RuO_4, the normal state near the superconducting transition is well described by a quasi-2D Landau-Fermi liquid (e.g., the resistivity in all directions follows a T^2 behavior for $T \lesssim 50$ K and the resistivity along and perpendicular to the c axis differ by a factor of 850 [1]). Quantum oscillations show three Fermi surface sheets with a 2D topology that agrees well with band structure calculations [2]. It has been pointed out [3] that the mass enhancement is similar to that of ^{3}He and that there is a metallic ferromagnetic phase in $SrRuO_3$ [4] (the 3D analog of Sr_2RuO_4). These observations indicate that an odd-parity ($l = 1$) superconducting state is likely [3]. This is consistent with the lack of a Hebel-Slichter peak in $1/T_1$ in nuclear quadrapole resonance (NQR) measurements [5]. A weak coupling analysis of the odd-parity state implies the gap should be of constant magnitude [3]. It is therefore surprising that specific heat [6] and NQR measurements [5] reveal that approximately 0.6 of the normal density of states remain in the superconducting phase in clean samples (those in which quantum oscillations were observed). As a consequence it has been proposed that an exotic nonunitary superconducting state similar to the ^{3}He A_1 phase is stabilized [7,8]. In this scheme, the normal state quasiparticle energy spontaneously splits into two branches (one for spin up and one for spin down) upon entering the superconducting state. One of these branches is gapped while the other is not, leading to a residual density of states that is half the normal density of states.

Here we propose an alternative explanation for the large residual density of states. The electronic properties near the Fermi surface of Sr_2RuO_4 are determined by Wannier functions with Ru d_{xy}, d_{xz}, and d_{yz} orbital character [9,10]. We show that the quasi-2D nature of the electronic dispersion implies that the bands are derived from either the xy or the $\{xz, yz\}$ Wannier functions and that the pair scattering amplitude between these two classes of bands will be significantly smaller than the intraclass pair scattering amplitude for any unconventional superconducting order parameters. It can therefore be expected that the gap on bands from one class is substantially smaller than that on bands from the other class. The presence of essentially gapless excitations for temperatures greater than the smaller gap will appear as a residual density of states. Also, the two classes may favor different superconducting symmetries in which case a second superconducting transition will appear at low temperatures.

Band structure calculations [9,10] give the correct shape of the Fermi surface, but predict an effective mass that is a factor of 4 smaller than that observed, indicating that strong coupling effects are important [2]. These calculations reveal that the density of states near the Fermi surface are due mainly to the four Ru $4d$ electrons in the t_{2g} orbitals. There is a strong hybridization of these orbitals with the O $2p$ orbitals giving rise to antibonding π^* bands. The resulting bands have three quasi-2D Fermi surface sheets labeled α, β, and γ (see Ref. [2]). The highly anisotropic nature of the Fermi liquid and the superconducting states suggests that the superconductivity essentially arises from intraplanar interactions, so we consider a single RuO_4 plane. The Hamiltonian describing the band structure of a plane is

$$H = \sum_{\nu,\nu',i,j,s} t_{\nu,\nu'}(\mathbf{R}_i - \mathbf{R}_j) c^{\dagger}_{\nu,i,s} c_{\nu',j,s}\,, \qquad (1)$$

where $c_{\nu,i,s}$ destroys an electron with spin s in the Wannier function centered at $\mathbf{R}_i$ that transforms as the Ru ν orbital ($\nu = \{xy, xz, yz\}$). Because of the σ_z reflection symmetry about the center of the RuO_4 plane $t_{xy,xz}(\mathbf{R}) = t_{xy,yz}(\mathbf{R}) = 0$. This implies that the γ sheet of the Fermi surface can be attributed solely to the xy Wannier functions while the α and β sheets are due to a hybridization of the $\{xz, yz\}$ Wannier functions. An effective Hamiltonian to describe the superconductivity is

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$$H = \sum_{l,\mathbf{k},s} \epsilon_l(\mathbf{k}) a^\dagger_{l,\mathbf{k},s} a_{l,\mathbf{k},s} + \sum_{l,l',\mathbf{k},\mathbf{k}',s,s'} [V_{l,l'}(\mathbf{k},\mathbf{k}') a^\dagger_{l,\mathbf{k},s} a^\dagger_{l,-\mathbf{k},s'} a_{l',-\mathbf{k}',s'} a_{l',\mathbf{k}',s} + \text{H.c.}], \quad (2)$$

where $a_{l,\mathbf{k},s}$ corresponds to the eigenoperators of Eq. (1) and

$$V_{l,l'}(\mathbf{k},\mathbf{k}') = \int d^3r\, d^3r' \sum_{j,j',n,n'} e^{i\mathbf{k}\cdot(\mathbf{R}_j - \mathbf{R}_{j'})} \phi^*_l(\mathbf{r} - \mathbf{R}_j) \phi^*_l(\mathbf{r}' - \mathbf{R}_{j'}) U(\mathbf{r},\mathbf{r}') e^{i\mathbf{k}'\cdot(\mathbf{R}_n - \mathbf{R}_{n'})} \phi_{l'}(\mathbf{r}' - \mathbf{R}_n) \phi_{l'}(\mathbf{r} - \mathbf{R}_{n'}), \quad (3)$$

where $U(\mathbf{r},\mathbf{r}')$ is an effective interaction and the spatial extent of the Wannier functions along the c axis restricts the integrations along z and z' to lie near the RuO_4 plane. For the matrix elements $V_{\gamma,\alpha}$ and $V_{\gamma,\beta}$ the symmetry of the Wannier functions under σ_z can be exploited to write

$$4U(\mathbf{r}_\perp, z; \mathbf{r}'_\perp, z') = 2U(\mathbf{r}_\perp, z; \mathbf{r}'_\perp, z') - U(\mathbf{r}_\perp, -z; \mathbf{r}'_\perp, z') - U(\mathbf{r}_\perp, z; \mathbf{r}'_\perp, -z'). \quad (4)$$

The z dependence of the xy Wannier functions limits the integrations along the z direction in the $V_{\gamma,\alpha}$ and $V_{\gamma,\beta}$ matrix elements to a distance on the order of $l/7$ [11] where l is the distance between two neighboring Ru ions. As a consequence, the lowest order term in a Taylor series expansion of Eq. (4) in $z/|\mathbf{r}_\perp|$ and $z'/|\mathbf{r}'_\perp|$ will give the largest contribution to $V_{\gamma,\alpha}$ and $V_{\gamma,\beta}$ for all but the on-site portion ($\mathbf{R}_j = \mathbf{R}_{j'} = \mathbf{R}_m = \mathbf{R}_{m'}$) in Eq. (3). The lowest nonzero term is of second order in this expansion. Since the on-site contribution is independent of $\mathbf{k}$ and $\mathbf{k}'$ it does not contribute to the effective coupling constant for any unconventional gap functions. It is therefore expected that the pair scattering amplitude between the γ sheet and the $\{\alpha,\beta\}$ sheets is significantly smaller than the intrasheet pair scattering amplitude (see Fig. 1). Furthermore, since the Wannier functions forming the two classes of bands are of different symmetry, the intrasheet pair scattering amplitudes will in general be different. We assume that the superconducting state is odd parity due to the considerations of Ref. [3]. Note that the simplest tight binding approximation to the band structure (in which the Ru $\{d_{xz}, d_{yz}\}$ orbitals overlap only with neighboring O p-π orbitals [9]) indicates that the gaps on the α and β sheets are the same magnitude for odd-parity pairing and we therefore assume that the gaps within this class have the same magnitude.

We consider a model in which the three Fermi surface sheets have densities of states as in Ref. [2]. We use a weak coupling approach and in accordance with the above considerations take $V_{l,l'}(\mathbf{k},\mathbf{k}') = U_{l,l'}\mathbf{k}\cdot\mathbf{k}'/(\langle k_x^2\rangle_l \langle k_x^2\rangle_{l'})^{1/2}$, where $\langle k_i^2\rangle_l$ is the average of k_i^2 on sheet l and

$$U = \begin{pmatrix} u_{xy} & u_m & u_m \\ u_m & u & u \\ u_m & u & u \end{pmatrix}, \quad (5)$$

where the matrix U operates on a basis with components that correspond to the Fermi surface sheets γ, α, β, respectively. Introducing the gap matrix

$$\Delta_{s_1,s_2}(l,\mathbf{k}) = \sum_{\mathbf{k}',l'} V_{l,l'}(\mathbf{k},\mathbf{k}') F_{s_1,s_2}(l',\mathbf{k}'), \quad (6)$$

where $F_{s_1,s_2}(l,\mathbf{k}) = \langle a_{l,\mathbf{k},s_1} a_{l,-\mathbf{k},s_2}\rangle$ gives rise to a mean field Hamiltonian that is diagonal in the band index. For an odd-parity interaction the gap can be expressed as $\hat{\Delta}(l,\mathbf{k}) = i[\mathbf{d}_l(\mathbf{k})\cdot\boldsymbol{\sigma}]\sigma_y$ [12]. For unitary states (the case considered here) the quasiparticle excitations are given by $E_{l,\mathbf{k}} = (\epsilon^2_{l,\mathbf{k}} + |\mathbf{d}_l(\mathbf{k})|^2)^{1/2}$ and the gap equation is given by

$$\mathbf{d}_l(\mathbf{k}) = \sum_{\mathbf{k}',l'} \frac{V_{l,l'}(\mathbf{k},\mathbf{k}')\mathbf{d}_{l'}(\mathbf{k}')}{2E_{l',\mathbf{k}'}} \tanh(\beta E_{l',\mathbf{k}'}/2). \quad (7)$$

Within weak coupling the transition temperature is $T_c = 1.13\epsilon_c \exp[-1/\lambda_{\max}]$, where $\lambda_{\max}$ is the largest eigenvalue of the matrix with components $U_{l,l'}(N_l N_{l'})^{1/2}$ and N_l is the density of states of sheet l. It has been assumed that the cutoff frequency ϵ_c is the same for all three bands.

The superconducting order parameter is $\mathbf{d}_l(\mathbf{k}) = \sum_{i,j} c_{l,i,j} k_i \hat{x}_j / \langle 2k_i^2\rangle_l$, which has a six fold degeneracy that is broken by spin-orbit coupling. The phases stabilized within weak coupling for the single band version of this model are the planar and the axial phases; both are degenerate within the approximations made above [7,13]. Spin-orbit coupling will prefer one of these two phases and will fix the spin orientation of this phase to the crystallographic axes, leading to the classification in Ref. [3]. The quasiparticle excitation spectra for the possible phases

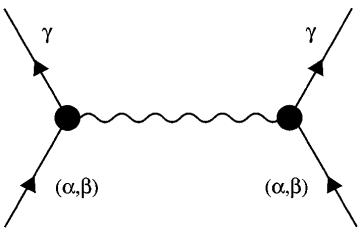

FIG. 1. The vertex leading to the pair scattering amplitude between the γ sheet and the other two sheets of the Fermi surface. The effective interaction for any unconventional gap symmetry due to this vertex is small in relation to intrasheet interactions.

are described by a gap of constant magnitude, so many properties will be correctly described by assuming that any one of these phases is stabilized. We assume that the A_{1u} phase, for which $\mathbf{d}_l(\mathbf{k}) = c_l(\hat{x}k_x + \hat{y}k_y)/\langle 2k_x^2\rangle^{1/2}$, is stabilized. The resulting gap equation for the $\{c_l\}$ then has the same form as that for isotropic superconductors generalized to include the presence of three bands [14].

The interaction parameters u_{xy}, u_m, and u remain to be specified. Earlier arguments imply $u_m \ll \max(u_{xy}, u)$ but the relation between u_{xy} and u remains unknown. Hund's rule ferromagnetic correlations between the Ru d_{xz} and d_{yz} orbitals may give rise to an increased odd-parity interaction for the $\{\alpha, \beta\}$ Fermi surface sheets. Also, the γ sheet is more 2D than the $\{\alpha, \beta\}$ sheets, so fluctuations may lead to a greater reduction in the T_c for the γ than for the $\{\alpha, \beta\}$ sheets. These considerations indicate that $u > u_{xy}$, so for illustration purposes we consider this to be the case (though it cannot be ruled out that $u_{xy} > u$ without a more detailed microscopic model). To show the qualitative behavior of this above model we take the density of states as measured in Ref. [2] (N_α:N_β:N_γ = 0.15:0.3:0.55) and the following values for the interaction matrix U: u_{xy}:u_m:u = 0.09:0.09:1.0 with $uN_\beta = 0.630$. Using for the specific heat C_{es}

$$C_{es} = -2k_B\beta^2 \sum_{l,\mathbf{k}} E_{l,\mathbf{k}} \frac{\partial f(E_{l,\mathbf{k}})}{\partial \beta}, \tag{8}$$

and solving the gap equation yields the gaps and the specific heat shown in Fig. 2. The presence of the small gap for the γ sheet gives rise to essentially gapless excitations for temperatures $T \gtrsim |\mathbf{d}_\gamma(\mathbf{k})|$ and this can give rise to the residual density of states observed experimentally. For temperatures below $|\mathbf{d}_\gamma|$, this gap gives rise to the low temperature exponential decay of C_{es}/T to zero. Note that the density of states is split approximately evenly between the γ sheet and the $\{\alpha, \beta\}$ sheets. Consequently, the smaller gap lying in either the γ or $\{\alpha, \beta\}$ sheets gives good agreement with the magnitude of the residual density of states seen experimentally. To show how the smaller gap manifests itself in other properties we have calculated the London penetration depth and the thermal conductivity in the basal plane (shown in Fig. 2). The London penetration depth is

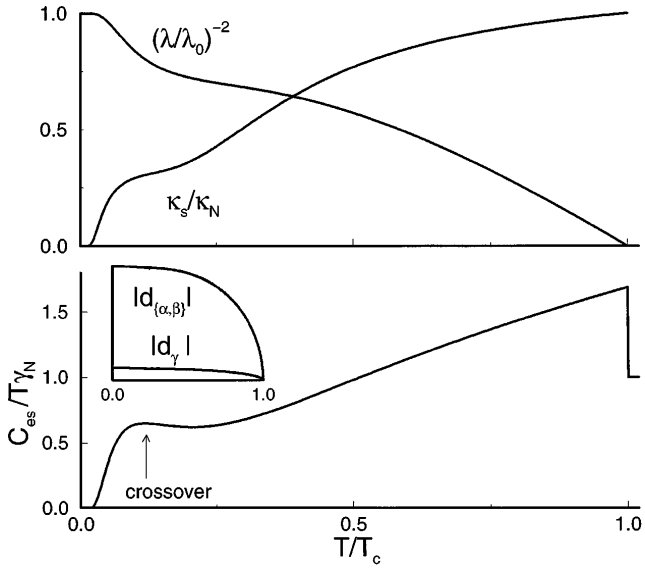

FIG. 2. Specific heat, London penetration depth, and thermal conductivity as a function of temperature. The inset shows the magnitude of the gaps $\mathbf{d}_\gamma$ and $\mathbf{d}_{\{\alpha,\beta\}}$ as a function of T/T_c.

$$\lambda_\perp^{-2}(T) = \frac{4\pi e^2}{c^2}\frac{1}{\Omega}\sum_{l,\mathbf{k}} v_{\perp,l,\mathbf{k}}^2 \left[\frac{\partial f(\epsilon_{l,\mathbf{k}})}{\partial \epsilon_{l,\mathbf{k}}} - \frac{\partial f(E_{l,\mathbf{k}})}{\partial E_{l,\mathbf{k}}}\right], \tag{9}$$

which results from a simple extension of the standard BCS expression to include many bands. The thermal conductivity in the single band case is derived in Ref. [15] and the suitable generalization to include many bands is

$$\kappa_\perp(T) = -2\sum_{l,\mathbf{k}} \frac{E_{l,\mathbf{k}}^2}{T} v_{\perp,l,\mathbf{k}}^2 \frac{\partial f(E_{l,\mathbf{k}})}{\partial E_{l,\mathbf{k}}} \tau_{l,\mathbf{k}} \tag{10}$$

with $\tau_{l,\mathbf{k}} = \tau_{N,l}|\epsilon_{l,\mathbf{k}}|/E_{l,\mathbf{k}}$ where τ_N is the normal state relaxation time. This form is valid within the Born approximation. It has been assumed that there is no interband scattering and that $\tau_{N,l} = \tau_N$. Note that $\tau_{l,\mathbf{k}}$ does not have the same form as that for a conventional isotropic superconductor due to the odd-parity coherence factors [16,17]. In calculating these properties it has been assumed that the density of states corresponds to that of a clean system. However it may be the case that while the large gap will remain intact in the presence of impurities the smaller gap may be rendered gapless (though there will still be a coherent pairing amplitude on this Fermi surface sheet [12]).

We have considered a model in which all the Fermi surface sheets favor the same superconducting symmetry. This model has two order parameters of the same symmetry [one (ψ_1) for the γ and one (ψ_2) for the $\{\alpha, \beta\}$ sheets] and can in principle have a second transition from a state in which $(\psi_1, \psi_2) = e^{i\theta}(|\epsilon_1|, \pm|\epsilon_2|)$ to a state in which time reversal symmetry is broken: $(\psi_1, \psi_2) = e^{i\theta}(|\epsilon_1|, e^{i\phi}|\epsilon_2|)$ where $\phi \neq 0, \pi$. An examination of the Ginzburg-Landau coefficients found by a weak coupling analysis shows that the broken time reversal symmetry phase does not occur in this model. However, as was considered by Leggett for the two band conventional superconductor [18] and more recently by Wu and Griffin in bilayer high T_c superconductors [19], there will exist a collective excitation corresponding to fluctuations into the broken time reversal symmetry phase (fluctuations of the relative phase of ψ_1 and ψ_2). If all orbitals favor the same pairing symmetry then such a mode may appear below the single particle threshold. This mode is in addition to those that were predicted to exist due to the odd-parity symmetry in the presence of weak spin-orbit coupling [3]. It is

also possible that due to the different symmetry properties of the xy and the $\{xz, yz\}$ Wannier functions the γ and $\{\alpha, \beta\}$ sheets may favor different superconducting symmetries. In this case a second superconducting transition (as opposed to the crossover behavior shown in Fig. 2) is likely to occur due to the smallness of the pair scattering amplitude between these two classes of sheets. A low temperature broken time reversal symmetry phase is possible within this scheme [12].

In conclusion, we have presented a model for the superconducting transition in Sr_2RuO_4 in which the superconductivity in the bands with Ru d_{xy} orbital character and the bands with Ru $\{d_{xz}, d_{yz}\}$ orbital character is weakly coupled. This model attributes the large observed residual density of states to thermal excitations across a secondary gap that is smaller than the primary gap driving the superconducting transition. This secondary gap should reveal itself in a wide variety of low temperature experiments on sufficiently clean samples. Also, within this model a second superconducting transition is possible. Experiments at very low temperatures are desirable to examine these possibilities.

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[1] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz, and F. Lichtenberg, Nature (London) **372,** 532 (1994).
[2] A. P. Mackenzie, S. R. Julian, A. J. Diver, G. G. Lonzarich, Y. Maeno, S. Nishizaki, and T. Fujita, Phys. Rev. Lett. **76**, 3786 (1996).
[3] T. M. Rice and M. Sigrist, J. Phys. Condens. Matter **7**, L643 (1995).
[4] T. C. Gibb, R. Greatrex, N. N. Greenwood, D. C. Puxley, and K. G. Snowden, J. Solid State Chem. **11**, 17 (1994).
[5] K. Ishida, Y. Kitaoka, K. Asayama, S. Ikeda, and T. Fujita (to be published).
[6] Y. Maeno, S. Nishizaki, K. Yoshida, S. Ikeda, and T. Fujita, J. Low Temp. Phys. **105**, 1577 (1997).
[7] M. Sigrist and M. E. Zhitomirsky, J. Phys. Soc. Jpn. **65**, 3452 (1996).
[8] K. Machida, M. Ozaki, and T. Ohmi, J. Phys. Soc. Jpn. **65**, 3720 (1996).
[9] T. Oguchi, Phys. Rev. B **51**, 1385 (1995).
[10] D. J. Singh, Phys. Rev. B **52**, 1358 (1995).
[11] This estimate is $\langle z^2 \rangle^{1/2}$ for a $4d_{xy}$ orbital with an effective charge $\tilde{Z} = 8$.
[12] M. Sigrist and K. Ueda, Rev. Mod. Phys. **63**, 239 (1991).
[13] V. I. Marchenko, Sov. Phys. JETP **66**, 79 (1987).
[14] H. Suhl, B. T. Matthias, and L. R. Walker, Phys. Rev. Lett. **3**, 552 (1959).
[15] B. Arfi and C. J. Pethick, Phys. Rev. B **38**, 2312 (1988).
[16] L. T. Coffey, T. M. Rice, and K. Ueda, J. Phys. C **18**, L813 (1985).
[17] C. J. Pethick and D. Pines, Phys. Rev. Lett. **57**, 118 (1986).
[18] A. J. Leggett, Prog. Theor. Phys. **36**, 901 (1966).
[19] W. C. Wu and A. Griffin, Phys. Rev. Lett. **74**, 158 (1995).